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(Commemoration Issue Dedicated to Professor Waichiro Tsuji On the Occasion of his Retirement)

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## **X-ray Small Angle Scattering Study on the Density of Interlamellar Regions of Drawn Polyethylene under Tensile Stress**

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The intensities of X-ray small angle scatterings from hot drawn high-density polyethylenes under the strains of elastic limit are measured. The changes in the intensities and the long periods by the strains lead to the conclusion that the density of polyethylene in interlamellar region is considerably lower than the melt density extrapolated to room temperature.

### **INTRODUCTION**

The nature of the so-called amorphous regions in crystalline polymers is still the subject of controversy among investigators. Several investigators measured the density of polyethylene specimens at room temperature with varying the degree of crystallinity.<sup>1-7)</sup> By extrapolating the density data to zero crystallinity, the density of the amorphous regions was estimated to be 0.85 g/cm<sup>3</sup>, nearly the same value which would be obtained by extrapolating melt density to room temperature.

Fischer, Goddar, and Schmidt<sup>8)</sup> also evaluated the densities of amorphous regions in both single crystals and highly stretched films of polyethylene by analysing the X-ray data by the Guinier and Fournet method.<sup>9)</sup> They obtained almost the same density as the extrapolated melt density for those in highly stretched films.

Kobayashi and Takahashi<sup>10)</sup> found that potassium bromide precipitated epitaxially on the surface of polyethylene single crystals. This finding suggests that the folding of polymer chains occurs in a regular way in the surface region of single crystals. Accordingly, the existence of liquid-like amorphous texture in polyethylene single crystals is seriously questioned. Recently, Shimamura and Kobayashi<sup>11)</sup> have observed on highly crystallized samples of polyethylene that the X-ray small-angle scattering intensities display a reversible change with varying temperature provided that the temperature is not raised too close to the melting point. The change is not affected by the method of preparation of the samples as illustrated in Fig. 1, where the open circles, closed circles and triangles represent the data obtained for single crystal mats, drawn films and melt-extruded films, respectively. All the data lie on a common curve representing the temperature dependence of the small-angle scattering intensity. This fact suggests that there is no essential difference among the textures of "amorphous" regions in these three types of samples. In this connection, we may refer to the recent study of Sullivan and Weeks<sup>12)</sup> on the X-ray scattering intensity of layer line from paraffine crystals. These investigators observed that

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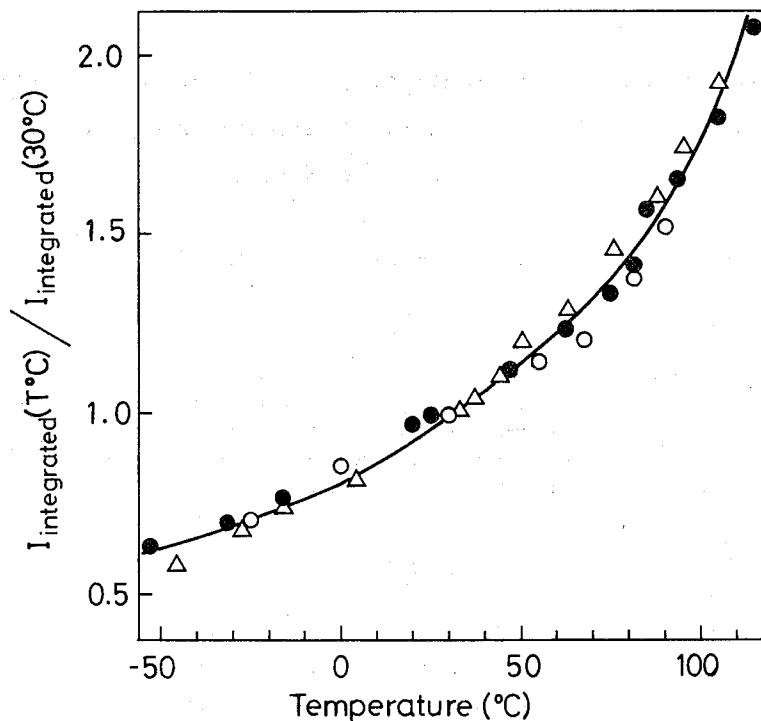


Fig. 1. Changes in the relative SAXS intensity with temperature.  
(△) drawn film, (●) extruded film, and (○) single crystal mat.

the X-ray scattering intensity changed reversibly with variation of temperature, and suggested that this change is caused by the formation of voids in the gap between molecular layers. The X-ray behavior of polyethylene crystals described above is quite similar in appearance to that of paraffine crystals, and hence it may be interpreted in the similar way. Thus, the view that the amorphous regions of polyethylene crystals have a liquid-like texture is again questioned.

In this paper, we intend to estimate the density of the "amorphous" regions of highly crystallized polyethylene by using a new method of small-angle X-ray analysis and to examine whether the density is the same as the extrapolated melt density or not.

## EXPERIMENTAL

### 1. Description of Specimens

Test specimens were prepared by drawing sheets of high density polyethylene (PE) about 700% at a rate of 10 mm/min at various temperatures in a liquid heating medium.

### 2. Measurement of the Small Angle X-ray Scattering (SAXS) Intensity

The SAXS patterns were recorded photographically and also by Geiger Müller (G.M.) counter method. Diffuse scattering due to slits was subtracted by ordinary procedures. Cu-radiation filtered through a nickel foil was used. Linearity of the G.M. counter was kept in the region less than 200 counts/sec.

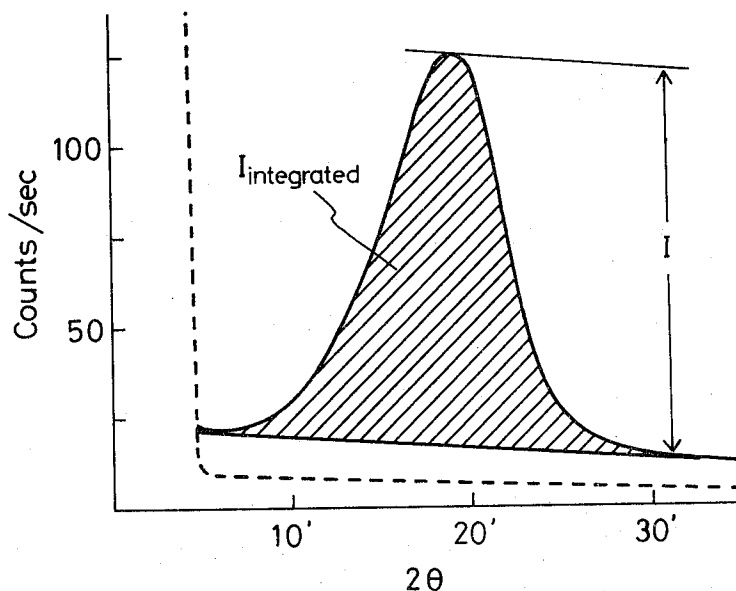


Fig. 2. Typical SAXS from a polyethylene specimen drawn at 110°C.

A SAXS goniometer was equipped with a device constructed for the measurement of SAXS intensity of a specimen under constant stress. The specimen was mounted horizontally between two clamps, which are properly situated as a specimen mount of the diffractometer. A constant weight was applied to the specimen by the use of a pulley. Long period of a specimen was determined by measuring 7 times the distance between the positions of maximum intensity of the first order SAXS and directly applying Bragg's law. The values were estimated with an experimental error of  $\pm 1.2 \text{ \AA}$ .

In the following discussion, we take only the characteristic discrete SAXS into consideration. The intensity  $I$  means the height of the intensity peak as shown in Fig. 2, and the integrated intensity is denoted by  $I_{\text{integrated}}$ . These intensities are the function of temperature  $T$  and stress  $S$ .

## RESULTS AND DISCUSSION

Electron microscopic observations have shown that a specimen drawn at 120°C has a lamellar structure on the surface which is similar in appearance as that observed on a sheet of melt-extruded film. The average thickness of the lamellae measured with an electron microscope was in agreement with the measured spacing from SAXS. On the other hand, a specimen drawn at 80°C shows no lamellae but only granular structure on its surface. However, the change in relative intensity of the discrete SAXS of this specimen with temperature  $I_{\text{integrated}}(T)/I_{\text{integrated}}(T_0)$ , was coincident with those of specimens with lamellar structure. This fact indicates that there exists a certain similarity between the structures of these specimens which are responsible for the SAXS. Such a speculation will be also supported by the following.

As is well-known, two kinds of deformation mechanisms of PE have been reported.<sup>13)</sup> During cold drawing, polymer chains in lamellae are subjected to complete unfolding as

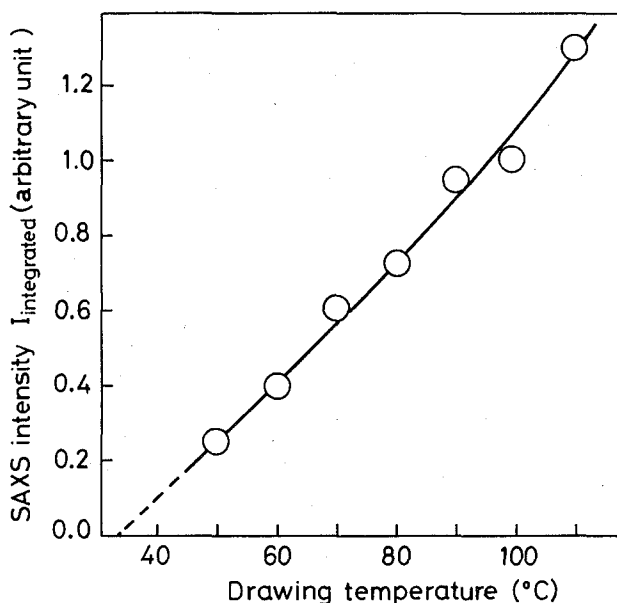


Fig. 3. Dependence of the SAXS intensity of drawn polyethylene on drawing temperature.

the chains are pulled out of the crystals. However, when the drawing temperature is high, it appears that the chains get only partially unfolded and the unfolded parts are pulled out from the original lamellae and incorporated in a new texture. These results are also shown by Tagawa *et al.*<sup>14)</sup> who tried to measure the fold content of drawn polyethylene by means of infrared method. Specimens drawn at high temperature gave discrete scattering on the meridian and no streaks on the equator. As shown in Fig. 3, the integrated intensity of the discrete scattering increases with the drawing temperature. On the other hand the patterns from specimens drawn at temperatures lower than 40°C show only a streak on the equator. These results are attributed to the fact that lamellae are the fundamental structural units which give the discrete SAXS.

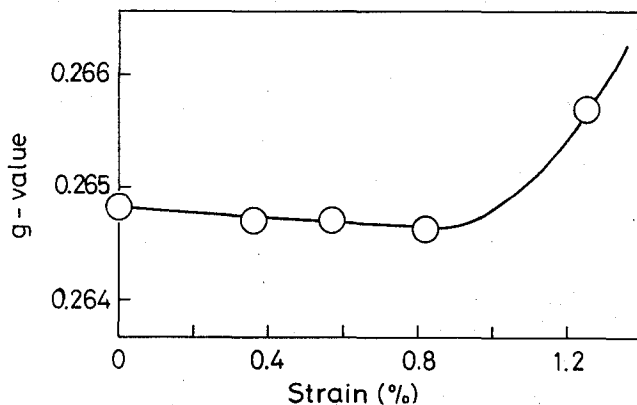


Fig. 4.  $g$ -value vs. strain

A film drawn at 110°C was stretched at room temperature, and it was found from the stress-strain curve that an elastic deformation occurred within the strain of 1.0%. From the positions of SAXS maximum and the half breadth of the peak, the  $g$ -value could be estimated on the paracrystalline theory of X-ray scattering.<sup>15)</sup> This value gives a measure of the fluctuation of structural periodicity along the fiber axis. In addition the intensity distribution of the discrete SAXS normal to the meridian could be obtained tilting the specimen to incident X-ray beam, as can be easily understood from Fig. 5. The lateral extent of a discrete scattering is generally interpreted as being a function of the unevenness and also the transverse dimension of the scattering units. In the elastic deformation, both the  $g$ -value and the degree of spreading of the discrete SAXS remained constant, *i.e.* any new microscopic disordering would not be introduced under these strains (Fig. 4, 6). In this case, the integrated intensity of the discrete SAXS is proportional to its height above the background level.

The change in the SAXS intensities and the long periods was reversible in a cycle of loading and unloading within a strain of about 1.0% (Fig. 7). These results made it possible to estimate the density and the thickness of interlamellar regions. Assuming that the mass in the interlamellar regions is unchanged whether the specimen is subjected to stress or not, one obtains

$$l_i^0 \cdot \rho_i^0 = (l_i^0 + \Delta l_i) \cdot \rho_i \quad (1)$$

where  $l_i^0$  and  $\rho_i^0$  are the thickness and the density of the interlamellar regions under no stress, respectively.  $\Delta l_i$  is an increase in the interlamellar thickness due to the stress and  $\rho_i$  is the density of the interlamellar regions under stress. Similarly in the crystalline region,

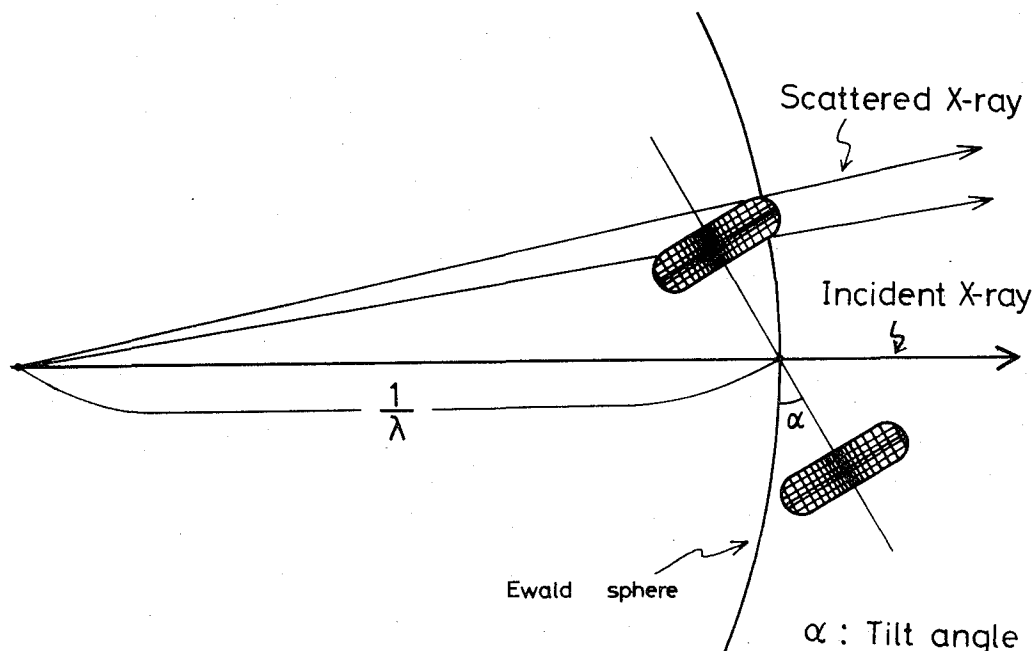


Fig. 5. Schematic diagram showing the principle of the measurement of the SAXS intensity distribution normal to the meridian by tilting the specimen.

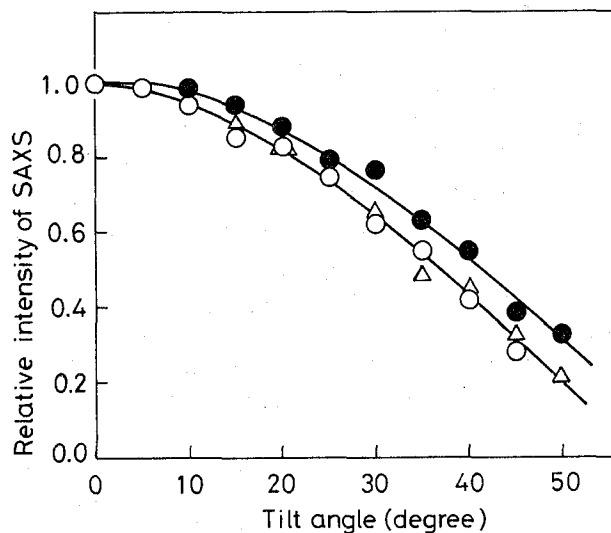


Fig. 6. Changes in the SAXS intensity as a function of tilt angle. (○) no strain, (△) elastic strain of 0.27%, and (●) plastic deformation of 4.2%.

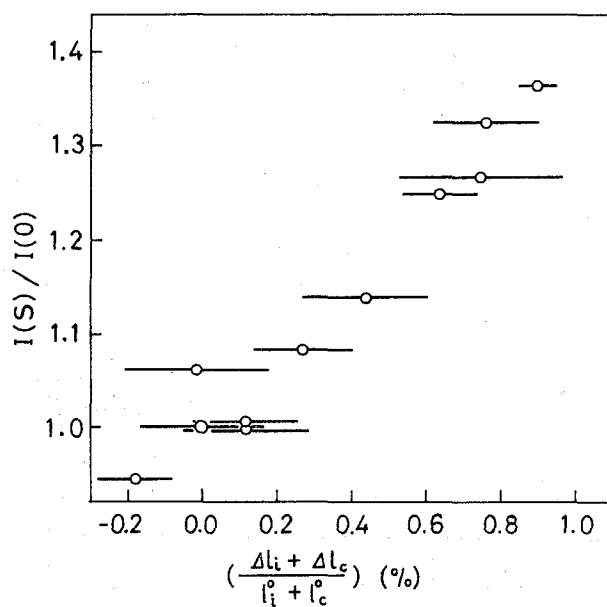


Fig. 7. Dependence of SAXS intensity on strain.

$$l_e^0 \cdot \rho_c^0 = (l_e^0 + \Delta l_e) \cdot \rho_c \quad (2)$$

The SAXS intensity by a system of stacking of lamellar crystals of various thickness is given by<sup>15)</sup>

$$I = K \cdot (\rho_c - \rho_i)^2 \cdot \sin^2(\pi b l_i) \cdot B(b)/b^2 \quad (3)$$

The relation is based on the premise that each interlamellar region has the same thickness.

Here  $\rho_c$  is the density of crystalline region and  $b = \sin \theta / \lambda$ , and  $K$  is independent of strain.  $B(b)$  is the interference function. Its value is determined by the interference between the scattered waves. Then from Eqs. (1), (2), and (3), one obtains

$$\left(\frac{I_s}{I_0}\right)^{1/2} = \frac{\left(\rho_c^\circ \frac{1_c^\circ}{1_c^\circ + \Delta 1_c} - \rho_i^\circ \frac{1_i^\circ}{1_c^\circ + \Delta 1_i}\right)}{(\rho_c^\circ - \rho_i^\circ)} \cdot \frac{\sin \pi b_s(1_i^\circ + \Delta 1_i)}{\sin \pi b_0 1_i^\circ} \cdot \left(\frac{B_s(b_s)}{B_0(b_0)}\right)^{1/2} \cdot \frac{b_0}{b_s} \quad (4)$$

where  $I_0$  and  $I_s$  are the scattering intensities by specimen under no stress and under stress, respectively.  $b_s$  and  $b_0$  are the values of  $b$  at maximum peak positions.

As shown above, the present experiments were carried out under the strain within the elastic limit, so that the regularity of the disposition of scattering units was kept unchanged whether the specimen was stressed or not. Hence,  $B_s(b_s)/B_0(b_0)$  may be assumed to be unity.  $\rho_c^\circ$  is obtained from the spacings of (002), (020), and (200).  $(1_c^\circ + 1_i^\circ)$  and  $(1_c^\circ + 1_i^\circ + \Delta 1)$  are also experimentally obtainable from the measurements of maximum positions of the SAXS (long period) where  $\Delta 1 = \Delta 1_c + \Delta 1_i$ . If we assume the value of  $1_i^\circ$ , the quantity  $1_c^\circ$  is obtainable from the long period.  $\Delta 1_c$  and  $\Delta 1_i$  can be determined separately from  $\Delta 1$  by the use of the crystal modulus along the  $c$ -axis. Thus, with assuming a set of values of  $\rho_i^\circ$  and  $1_i^\circ$ , we can calculate from Equation 4 the quantity  $(I_s/I_0)^{1/2}$  as a function of the strain  $\Delta 1$ . The relative mean deviation of the calculated curve of

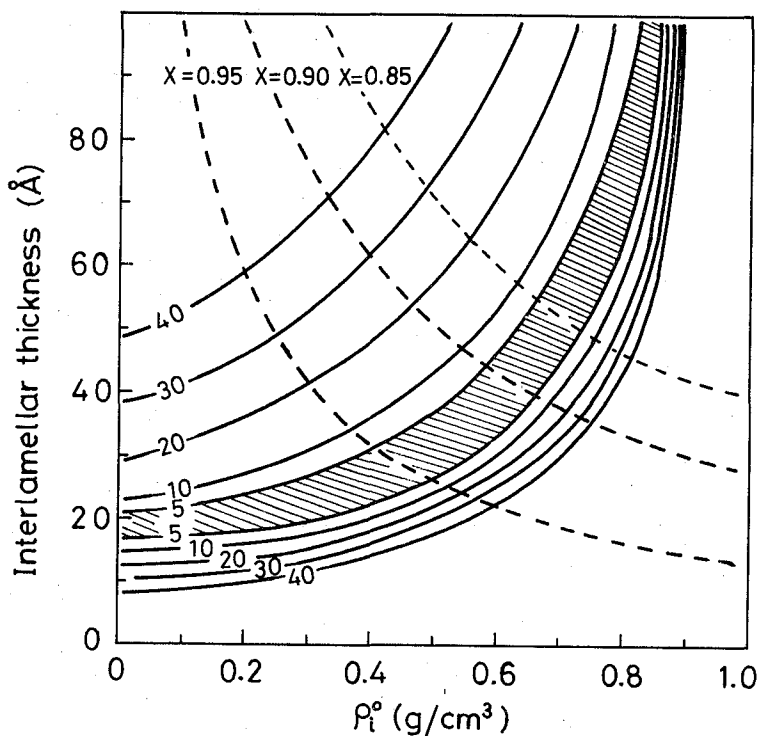


Fig. 8. A contour map of the relative mean deviations of the calculated SAXS intensity from the observed values as a function of  $\rho_i^\circ$  and  $1_i^\circ$ . The dotted line shows the relation of  $1_i^\circ$  and  $\rho_i^\circ$  for different crystallinities according to Eq. (5).



$(I_s/I_o)^{1/2}$  vs.  $\Delta l$  from the experimental one was then evaluated for each given set of  $\rho_i^\circ$  and  $l_i^\circ$  values. Figure 8 gives a contour map of the mean deviation thus evaluated, where the numbers attached to the contours (solid curves) represent the percentage deviation. Thus, each point in the shaded region corresponds to a possible set of  $\rho_i^\circ$  and  $l_i^\circ$  values which leads to the calculated curve for  $(I_s/I_o)^{1/2}$  vs.  $\Delta l$  within a 5%-deviation from the experimental one. Then, if  $l_i^\circ$  is known from other source of experiments, the density of "amorphous" region  $\rho_i^\circ$  can be determined from the figure. Such an information or  $l_i^\circ$  may be obtained from the degree of crystallinity as shown below.

It has been already pointed out that there are many disorders in polymer crystals.<sup>17)</sup> Such disorders will decrease the intensity of crystalline scatterings. Ruland<sup>18)</sup> was the first who tried to take account of such effects in evaluating the degree of crystallinity of polypropylene. Recently his method was also applied to polyethylene by Katsura,<sup>19)</sup> who showed that the degree of crystallinity by Ruland's method was generally several percents larger than that estimated by the ordinary wide angle X-ray method. Unfortunately, Ruland's method can not be applied to oriented specimens. Therefore, we evaluate first the crystallinity of the sample by the ordinary method, and obtained a crystallinity of about 85%. Then, the degree of crystallinity according to Ruland's method may be estimated to be over 90%.

The SAXS is caused by the electron density fluctuation on a scale of several ten to several thousand angstroms, that is, the SAXS is not influenced by the disorders such as point defects and thermal agitation in crystalline regions, because these defects do not change the density so much. Therefore,  $l_c^\circ$  in Eq. (2), the thickness of lamellae, must include the thickness of highly disordered region, if any, which is in the vicinity of the surface of the lamellae and has nearly the same density as the crystal. The degree of crystallinity is defined as

$$X = \frac{\rho_c^\circ l_c^\circ}{\rho_i^\circ l_i^\circ + \rho_c^\circ l_c^\circ} \quad (5)$$

Putting  $l^\circ = l_i^\circ + l_c^\circ$ , we obtain

$$l_i^\circ = \frac{\rho_c^\circ (1-X) l^\circ}{\rho_i^\circ X + \rho_c^\circ (1-X)} \quad (6)$$

As already mentioned,  $\rho_c^\circ$  and  $l^\circ$  are experimentally determinable. Hence, if we assign a value for X Eq. (6) gives a hyperbola in the  $l_i^\circ$  and  $\rho_i^\circ$  diagram. This is shown in Fig. 8 by the dotted lines where the attached numbers represent the assumed value X. Now, X of the present sample is higher than 0.90 as mentioned above, we find that the density of the interlamellar region is lower than 0.65 g/cm<sup>3</sup>.

The interlamellar density may be estimated also from a different point of view. It was determined from the SAXS that the specimen has a long period of 280Å. On the other hand the thickness of the crystalline region along the  $c$ -axis is evaluated to be 216Å from the longitudinal breadth of a wide angle meridional reflection (002) with the aid of the Scherrer's equation.<sup>21)</sup> However, the thickness is underestimated by this method because the diffraction line tends to broaden owing to crystal distortion. The conformation of chains within the fold causes large stress and the strain will penetrate into lamellae. Recently Oyama<sup>22)</sup> has calculated the depth of the penetration. About seven CH<sub>2</sub> units

from the lamellar surface are obliged to deviate from their ideal positions. The density of the region is not changed by this effect, but the crystallite length along the  $c$ -axis is decreased as large as  $10\text{\AA}$ . In addition, the folding region occupies about  $6\text{\AA}$  in length. The thickness of the lamellae with the density of  $0.99\text{ g/cm}^3$  become  $216 + (10 + 6) \times 2 = 248\text{\AA}$ . Consequently, the thickness left for the interlamellar region is about  $30\text{\AA}$ , which indicates that the density of the interlamellar region is smaller than  $0.6\text{ g/cm}^3$  from Fig. 8.

Fischer *et al.* reported densities higher than  $0.85\text{ g/cm}^3$  for interlamellar regions of various drawn polyethylene. They have measured the absolute scattering intensities in the reciprocal space within small angle region and adopted the principle of conservation of scattered intensity. In addition, they assumed that the whole volume of the specimen contributed to the SAXS for the evaluation of the interlamellar density. However, this assumption is not valid, because there may be some regions which have no lamellar structure and do not contribute to the SAXS. Thus, the density of the interlamellar regions obtained by Fischer *et al.* may be somewhat overestimated. On the contrary, our method for the evaluation of the interlamellar density is not influenced by the presence of such regions which do not contribute to the SAXS.

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